

Boundary depth of aragonite saturation during 10 years around Okinawa and East China Sea

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Introduction

Since industrial evolution, anthropogenic activities have been releasing CO₂ by fossil fuels combustion. Ocean absorbs about 2.0 Gt of CO₂ every year and act as a sink for atmospheric CO₂ [1]. However CO₂ dissolved into seawater lower the ocean pH and CO₃²⁻ concentration. About 0.1 pH unit has already been decreased since industrial evolution. Lower pH have influences on marine organisms especially on growth of calcareous foraminifera and corals as one of the problem in "ocean acidification". Because lower CO₃²⁻ caused lower aragonite saturation of CaCO₃, saturated boundary in the ocean is predicted to be shallower in the future. In this study, we investigated carbonate system by taking vertical profiles around Okinawa and East China Sea to find the shift of the boundary depth over the past 10 years.

Materials and Methods

Seawater samples were taken from East China Sea and adjacent sea around Okinawa Island, Japan at scientific survey of T/S *Nagasaki-maru* in 2000 to 2010. Parameters related to carbonate system were measured on total alkalinity (ATT05, Kimoto), total inorganic carbon (CM5012, UIC), pH and salinity (PortaSal8410A, Guildline). Aragonite saturation of CaCO₃ (Ω) was estimated from a calculation of carbonate chemical equilibrium in seawater samples taken at each depth of vertical profile.

Results and Discussion

The boundary depth at which aragonite saturation shows below a saturation level (i.e. $\Omega=1$) were 537±36 m from a surface (averaged value during 2000-2002). This boundary depth was shifted to 513 m during 10 years. Although this value was within the range of uncertainties, the shift indicated that the intrusion of the anthropogenic CO₂ caused lower CO₃²⁻ and hence shallower depth of the saturation boundary.

[1] Takahashi *et al.* (2002) *Deep-Sea Res. II* **49**, 1601-1622.

Study of geochemical reaction of rocks the under the supercritical CO₂-rock-groundwater system

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Laboratory scale experiments to quantify the geochemical reaction in the supercritical CO₂-rock-groundwater system for CO₂ sequestration sites were performed in the high-pressure cell. Seven types of rocks were cut into 1 cm x 1 cm x 0.3 cm size sections. Polished rock sections (granite, basalt, andesite, gneiss, limestone, sandstone and mudstone) and groundwater of 100 ml were reacted with supercritical CO₂ in the cell, maintaining the sequestration condition (100 bar and 50 °C). The gaseous CO₂ (99.99 % of purity) was injected into the cell and the high pressure condition was applied inside of the cell by using the periodic high pressure pump and the back pressure regulator. The temperature of the cell was maintained at 50 °C by using an oven. Each rock section was reacted with the supercritical CO₂ and groundwater for 10, 30 and 60 days.

Before the experiment, the rock dried at 100 °C for a day and accurately weighed. After the reaction, the rock dried and reweighed to investigate the loss of minerals by dissolution. The alteration of pH was measured to compare before/after reaction. Rock surface was observed by using a reflecting microscope. Selected three minerals for each rock and three locations of each mineral on the rock surface were randomly selected for the image analysis of Scanning Probe Microscope (SPM). The average roughness value of those locations was measured to investigate the transmutation of rock surface compared to that before reaction. ICP-OES analysis was conducted to measure the major element concentrations dissolved in solution of the high pressure cell. SEM/EDS analysis was also performed to identify the precipitates in high pressure cell after the reaction.

Results of the experiment in the supercritical CO₂-rock-groundwater reaction showed that the concentration of cations in solution increased and the pH of solution decreased after the reaction. The average roughness value of the mineral surface in the rocks increased after 30 days. From the analysis of SEM/EDS, the interstitial spaces of rock surface could be infilled by secondary minerals, resulting in the change of void spaces (porosity) in the rock.